Aligned Boron Nitride Nanotube Forests for Thermal Management

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NASA Aeronautics Research Mission Directorate (ARMD)

2014 Seedling Technical Seminar

February 19–27, 2014

Outline

- Innovation –objective of the work
- Impact of the innovation if it is eventually implemented
- Technical approach
  - Processing/equipment
  - Substrates
  - catalysts
- Results of the Seedling effort to date
- Distribution/Dissemination
- Next steps

The Innovation – Aligned BNNT Forests

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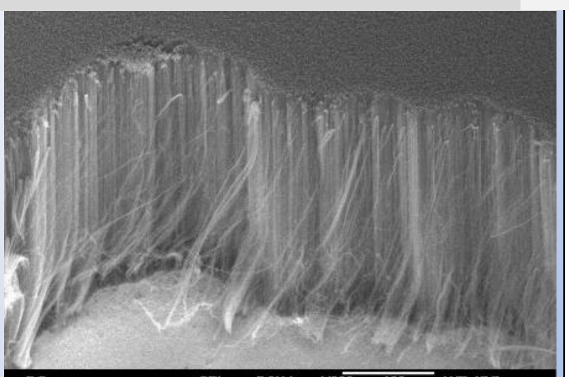
Objective of the innovation - *to establish the feasibility of growing aligned BNNT forests that can be applied as thermal interface materials between heat source and heat sink in an efficient thermal management system.*

Aligned CNT nanoforests have been demonstrated and are commercially available.
BNNT is much more difficult to synthesize.

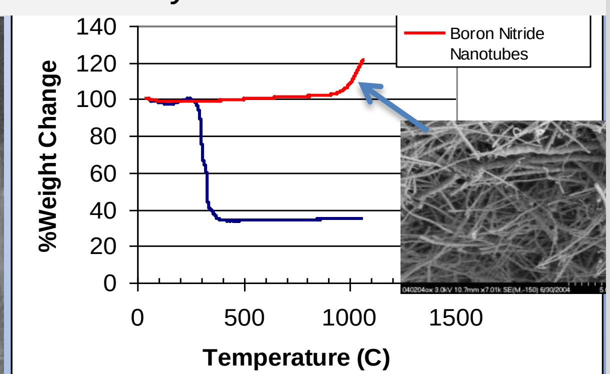
BNNT is a much more thermo-mechanically stable material than CNT.
Stable to 1000C in air.

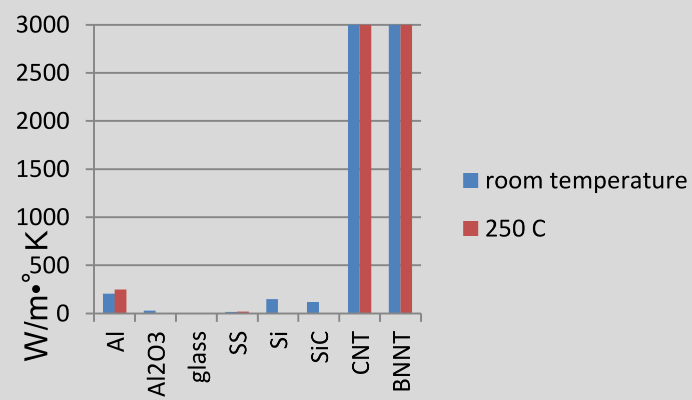
BNNT is unique in that it has ***high*** thermal conductivity while also having a ***low*** electrical conductivity.

Commercially available CNT forest from Nanocomp



Thermal Stability by Thermogravimetric Analysis of BNNT and CNT





Impact

- Hybrid electric propulsion system may be needed to meet NASA's long-term aggressive fuel burn and emission goals for N+3 and N+4 timeframes.
- Electrical systems for hybrid electric propulsion will require 3-4X increase in power density in electrical components. Power management and distribution of large amount of power in hybrid electric propulsion system will require high power density power electronics, which is currently limited by thermal management.
- Also near term benefits for airplanes
  - Growing need to increase the power density of power electronic components arising from more electric architectures.
  - With increasing use of polymer composite structures (which have lower thermal conductivity than metallic structures) in airplanes, thermal management for high power density power electronics has become a challenge.
  - Alternate methods of thermal management, such as cooling tubes, heat pipes, and phase change materials add significant weight to the system, which makes aligned nanotube-based thermal management system very attractive. The proposed effort would enable high power density electrical components and power electronics without any weight penalty.

- This BNNT aligned forest technology could be incorporated into current thermal management systems with little change and no weight penalty. For example, the BNNT nanoforests can be grown on the back of a Si chip that is typically used in power electronics. Similarly, BNNT forests can be sandwiched between the heat source and sink. The application of aligned BNNT forests would require an additional processing step for thermal management applications.

Literature search

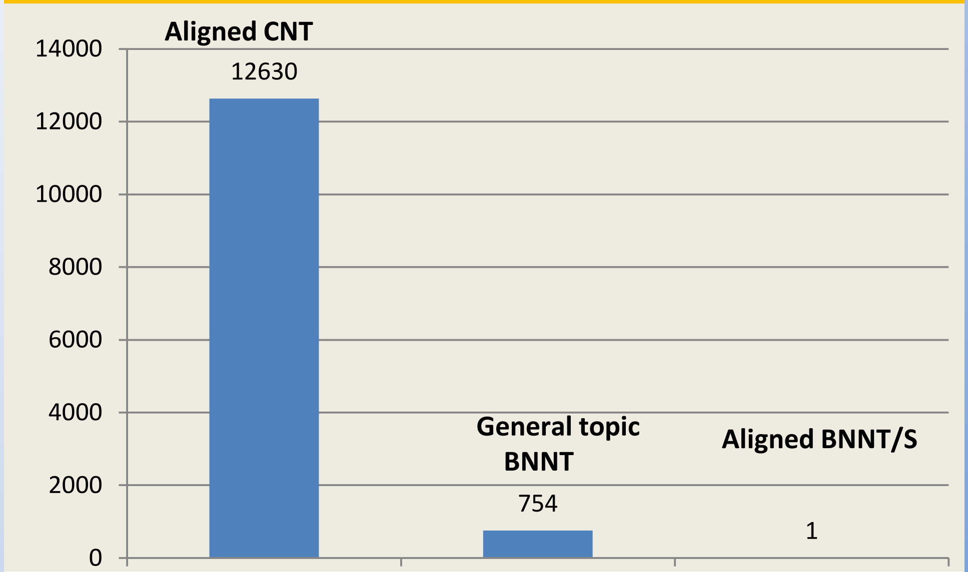
Literature:

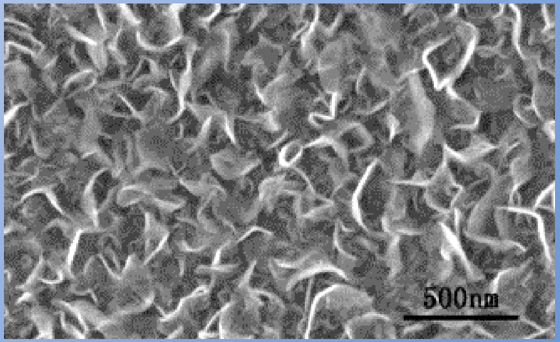
[Synthesis of vertically aligned boron nitride nanosheets using CVD method]

Materials Research Bulletin, *Volume 47, Issue 9*, *September 2012*, *Pages 2277-2281*

Chao Zhang, Xiaopeng Hao, Yongzhong Wu, Miao Du

Number of publications in Science Direct





$BCl_3–NH_3–H_2–N_2$

Technical approach

Catalytic chemical vapor deposition process similar to successful VACNT processes

- Evaluate suitability of several substrates
- Catalyst particles (Fe, Zn, Oxides, etc) are deposited on substrates (SiC, Si, C, Al_2O_3) prior to BNNT growth. Synthesis of patterned catalyst templates to create equidistance straight nanotubes of identical length on a substrates (Si, SiC, C, Al_2O_3, 304 stainless steel, superalloy).

- Catalyst thickness as well as density, phases, and defect concentration within the catalyst all substantially effect nanotube growth. Gas environments and substrate orientation, grain size, etc.

Desired Outcome -

- Evaluate feasibility of BNNT forest growth
- Identify critical issues for BNNT forest growth
- Identify path for development of BNNT forests

Aligned Boron Nitride Nanotube Forests for Thermal Management

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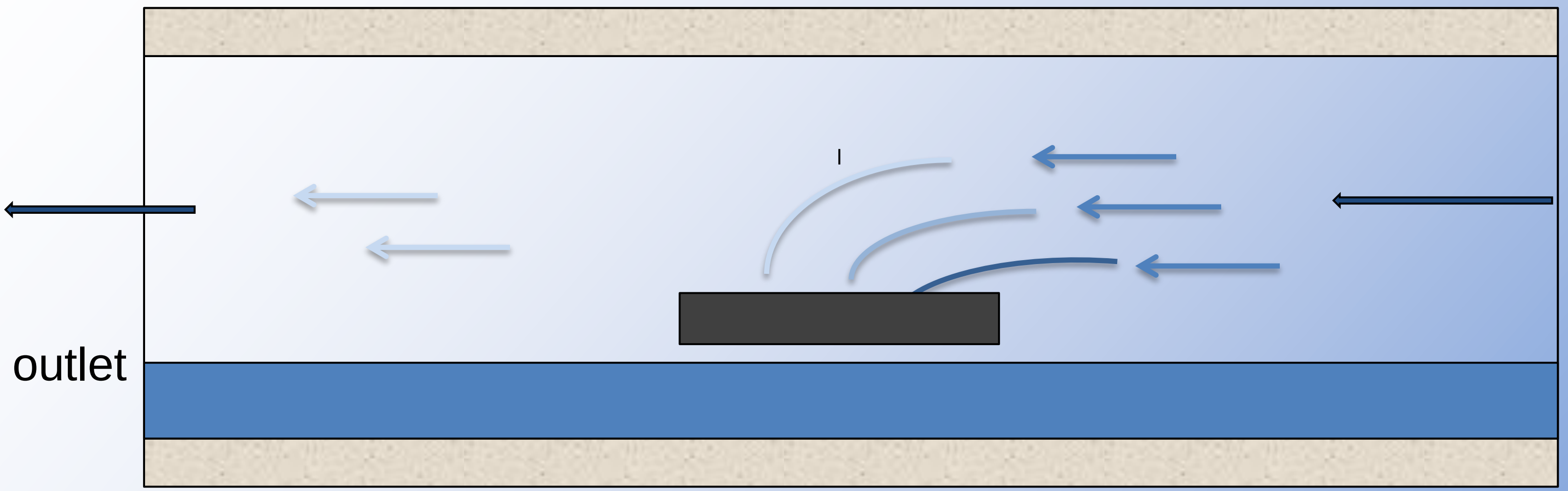
Proposed schedule

Tasks	Q1	Q2	Q3	Q4
Substrate/NT compatibility	**x**			
Selection promoter/catalyst	**x**			
Effect of catalysts				
& thickness/pattern density		**x**	**x**	
2nd Iteration		**x**	**x**	
Thermal testing/characterization			**x**	**x**
Deliverable preparation				**x**

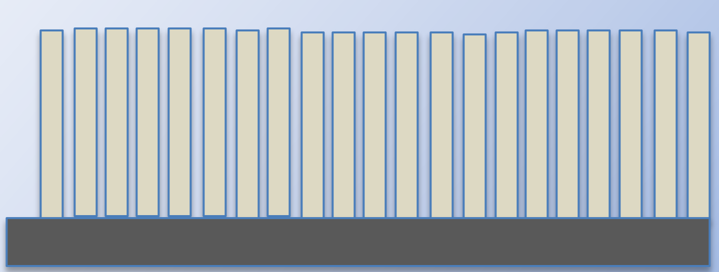
Actual schedule

	Q1	Q2	Q3	Q4
Substrate/NT compatibility	x			
Rig redesign	x			
Calibration runs				
Substrate/NT compatibility		x		
Rig redesign		x		
Calibration runs			x	
Catalyst/matrix effects		x	x	x

Line 1

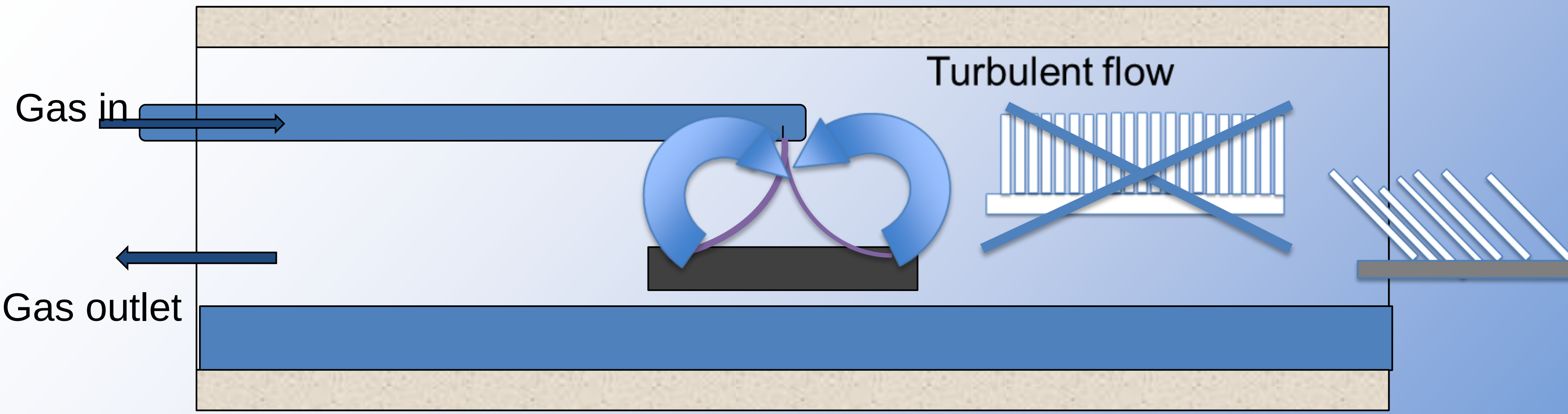


Variables –
Work piece location
Processing gas flows – and changing composition of gases
Temperature
Time

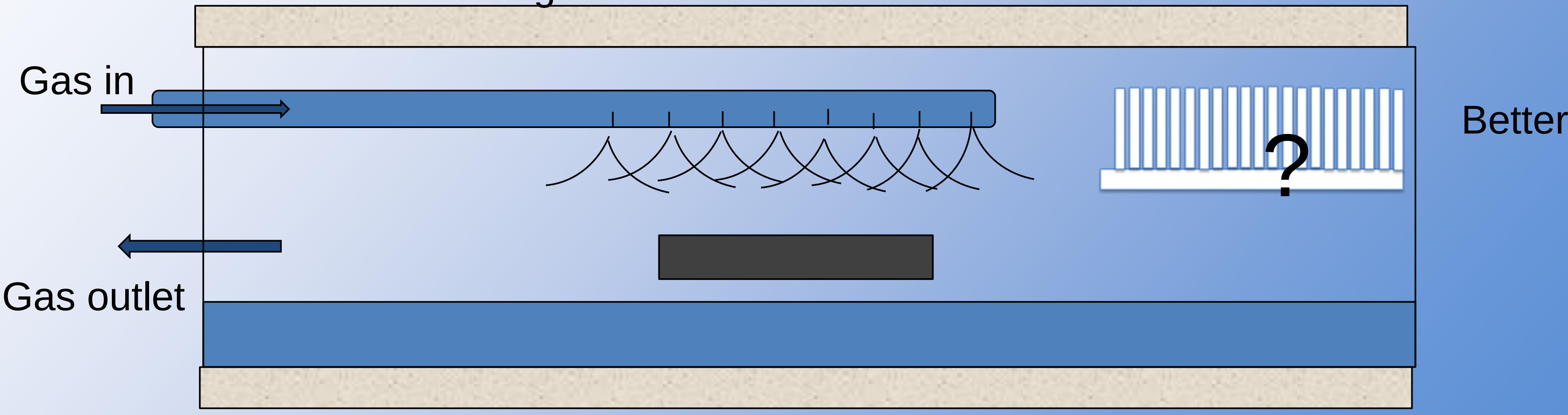


goal

Line 1



Line 2 – Modified for even gas distribution



Aligned Boron Nitride Nanotube Forests for Thermal Management

Technical Progress & Accomplishment

- Electrochemical deposition rig built.
- Alterations to BNNT Line 2 finished.
- Check outs and optimization of processing parameters finished. Development of processing maps completed.
- Investigations of substrates alone.
- Found compatibility with SiC, Si, superalloy substrates. Problems with alumina –requires catalyst.
- Found little difference in growth from substrate orientation effects for Si – 001 vs 111
- Demonstrated aligned nanoforest growth on SiC and superalloy in limited areas.
- Growth of BNNT on Si was demonstrated but with less alignment
- Abundant semi-aligned growth on SiC, superalloy, Si

Test matrix on modified rig 2

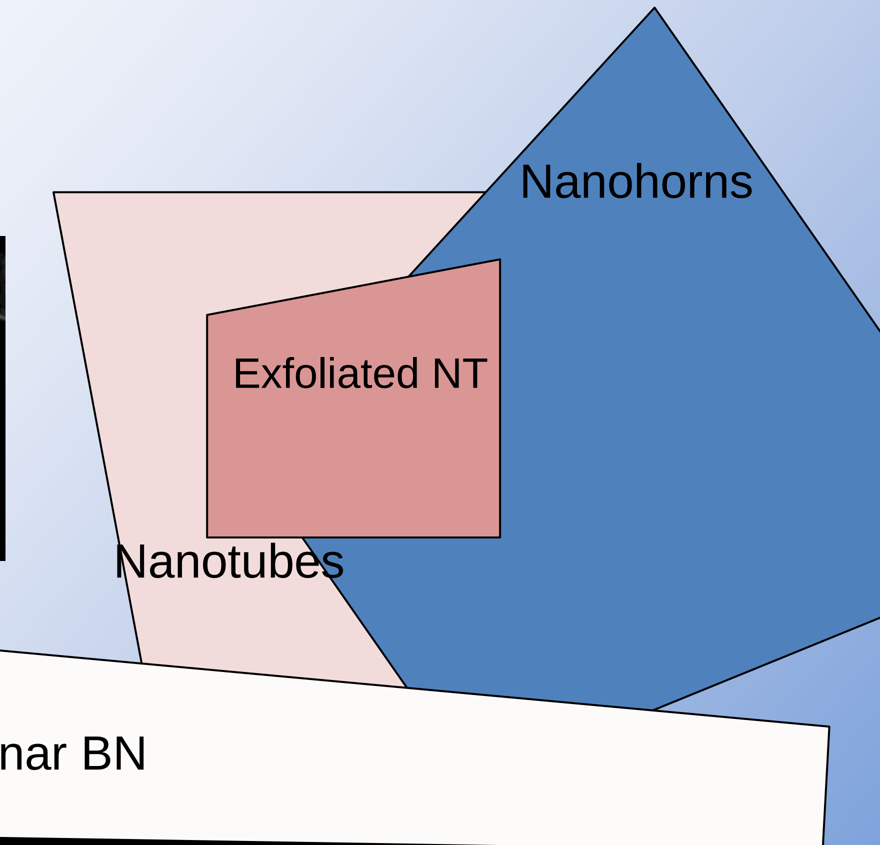
	SiC -1	SiC-2	SiC-3	SiC-4	Si	Si	SS	Al2O3	C	runs
position	2	3	3	3	2	2	2	2	2	21
temp	3	2	2	2	2	2	2	2	2	19
time	2	2	2	2	2	2	2	2	2	18
catalyst1	1	1	1	1	1	4		1	1	8
catalyst 2	4				4	4		1	4	17
catalyst3	2				1	2			2	7
misc										30
runs										120

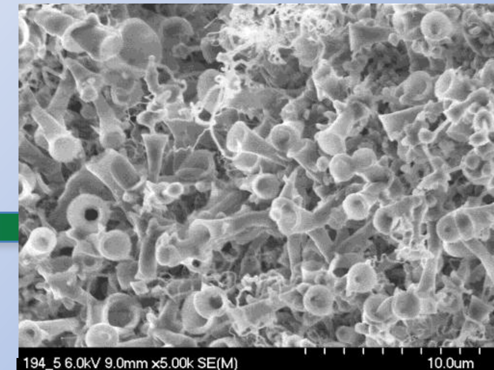
120 runs = 120 rig days or 30 weeks

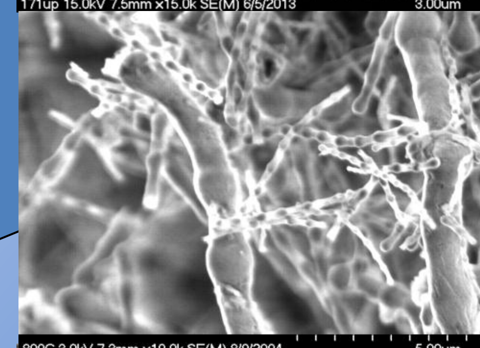
Draft Processing Diagrams

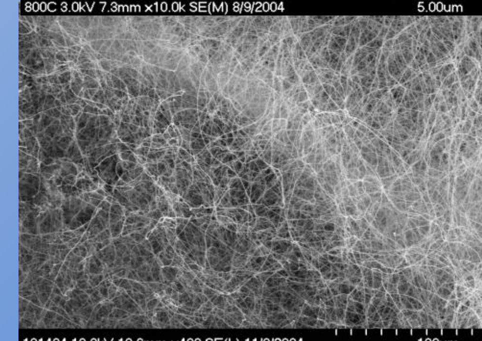
$NH_3 + B_2O_3 \rightarrow BO_x \rightarrow BN_x \rightarrow BN + H_2O$

Oxide has critical role as a reaction promoter –









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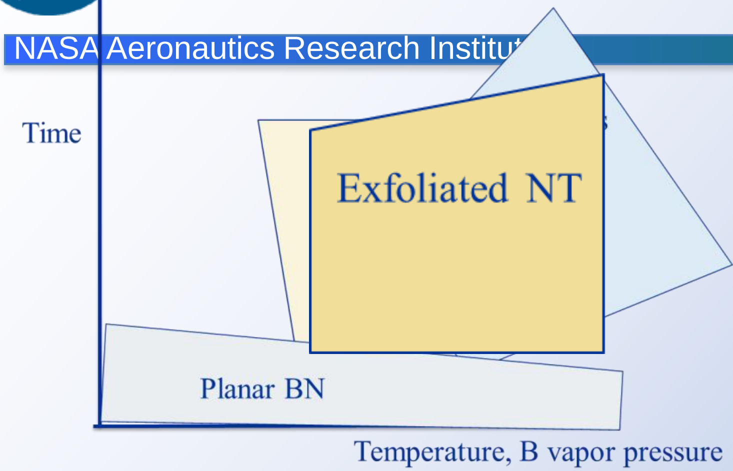
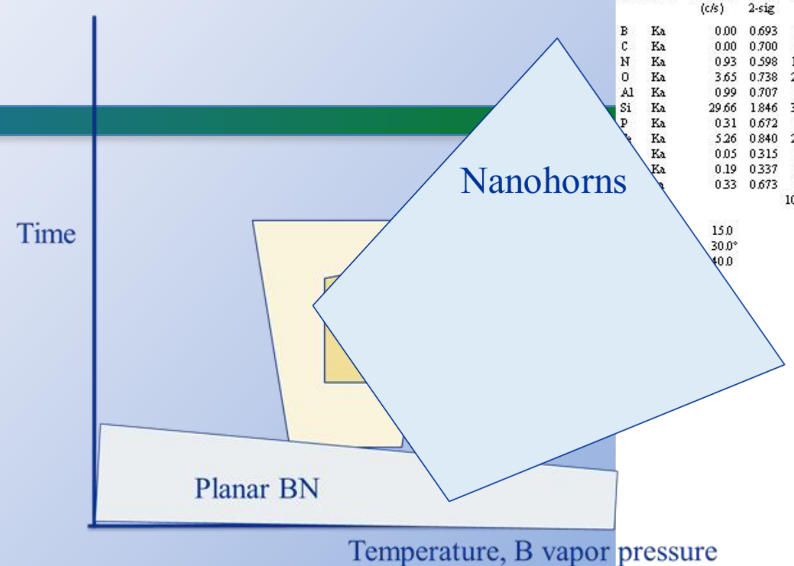
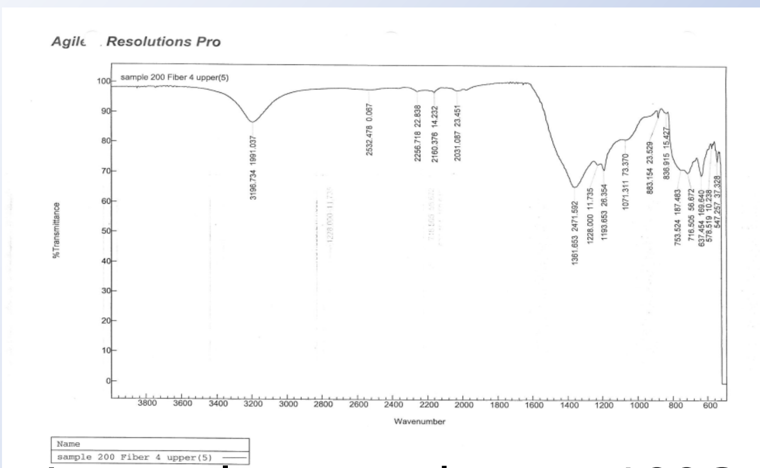




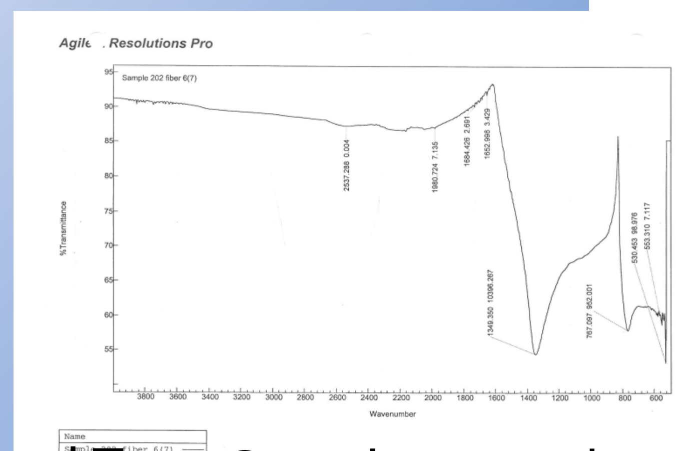
Elt.	Line	Intensity (c/s)	Error 2-sig	Conc	Units	
B	Ka	0.00	0.693	0.000	wt.%	
C	Ka	0.00	0.700	0.000	wt.%	
N	Ka	0.93	0.598	12.958	wt.%	
O	Ka	3.65	0.738	24.725	wt.%	
Al	Ka	0.99	0.707	1.293	wt.%	
Si	Ka	29.66	1.846	35.561	wt.%	
P	Ka	0.31	0.672	0.523	wt.%	
[illegible]	Ka	5.26	0.840	20.697	wt.%	
[illegible]	Ka	0.05	0.315	0.384	wt.%	
[illegible]	Ka	0.19	0.337	2.139	wt.%	
[illegible]	[illegible]	0.33	0.673	1.720	wt.%	
				100.000	wt.%	To
		15.0				
		30.0°				
		40.0				

Effect of impurity concentration – Si

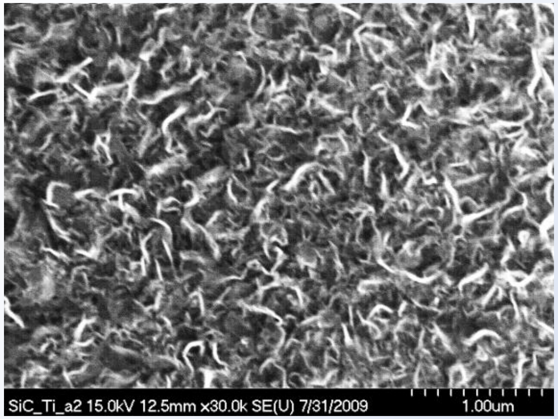
?Effect of impurity concentration – Mg,

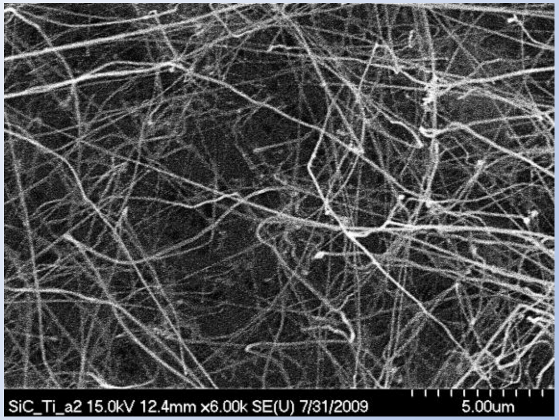


Incomplete reaction –at 100C reduced T



Complete reaction –





Effect of increasing gas velocity

Silicon substrate with Ti

Results of the Seedling

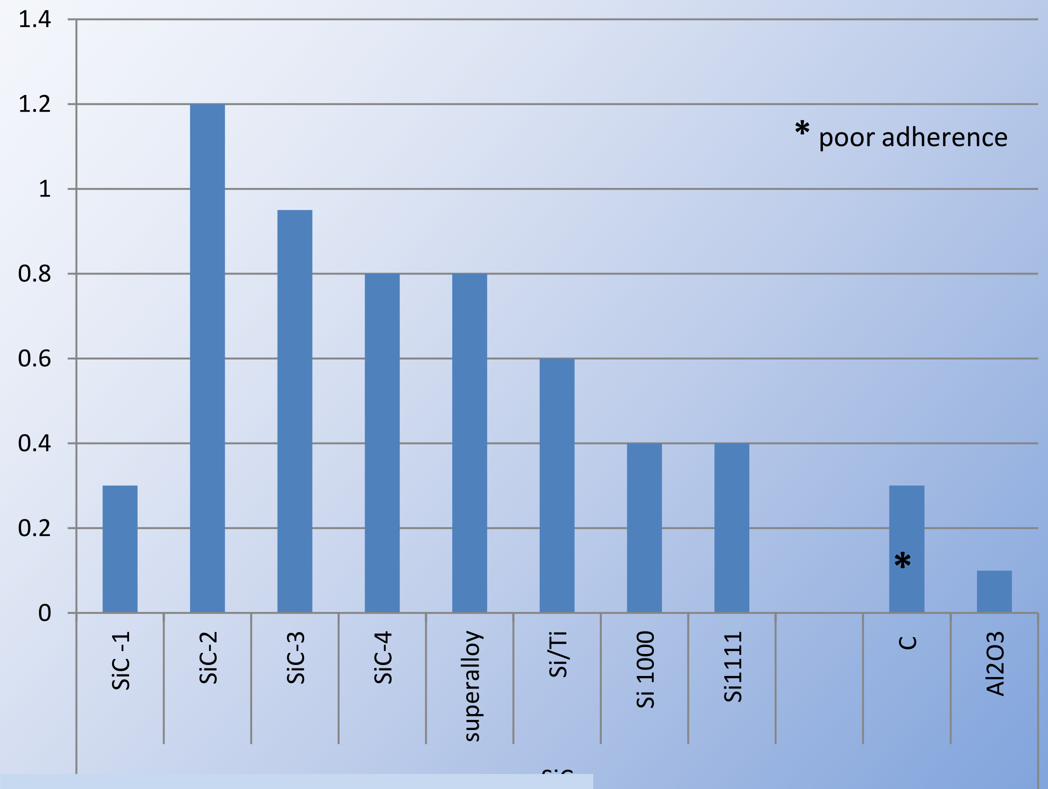
Substrate Summary – highest to lowest BNNT abundance

Substrate alone

- **Superalloys – FeCrAlY – abundant growth**
- **SiC – abundant semi-aligned growth, dependent upon surface.**
  ~ALIGNED growth with combination of catalyst/pretreatment
- Silicon – growth unaffected by 1000 versus 1111. Catalyst improved growth.
  small amount of ALIGNED growth with combination of catalyst/pretreatment
- Carbon – semi-aligned growth
- Al_2O_3 – poor growth w/o catalyst. V-V growth over substrate. Growth with catalyst is possible.

Matrices

Normalized
Weight gain



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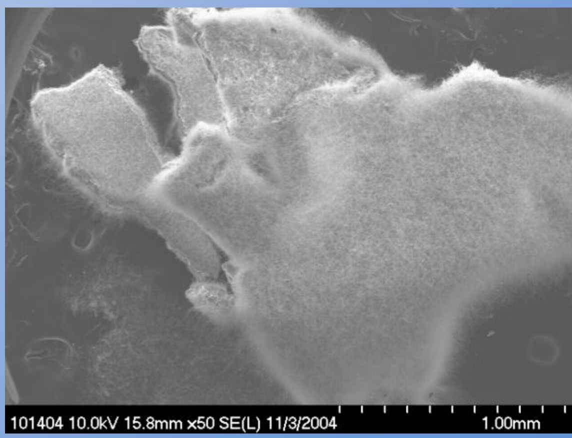
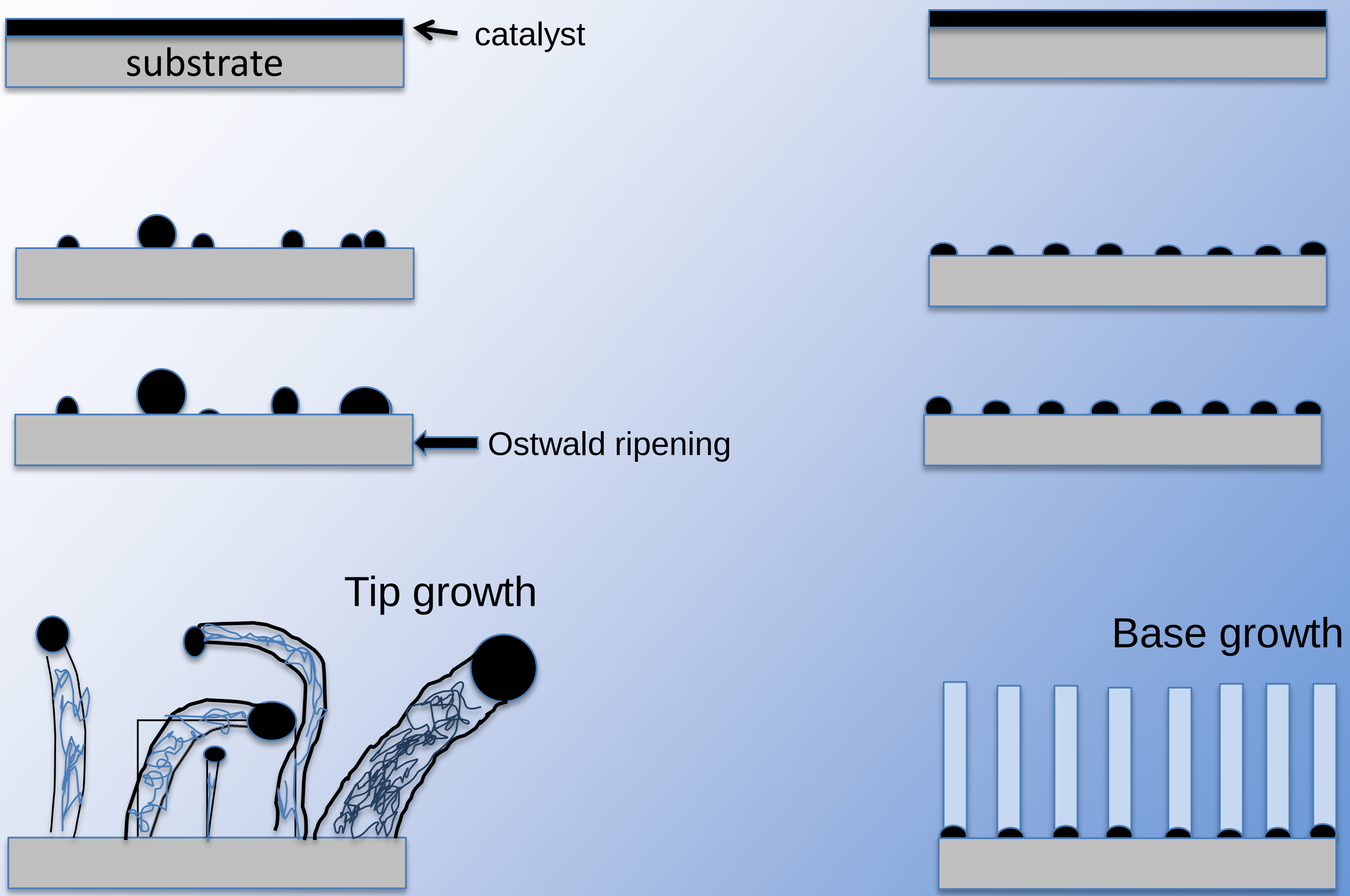
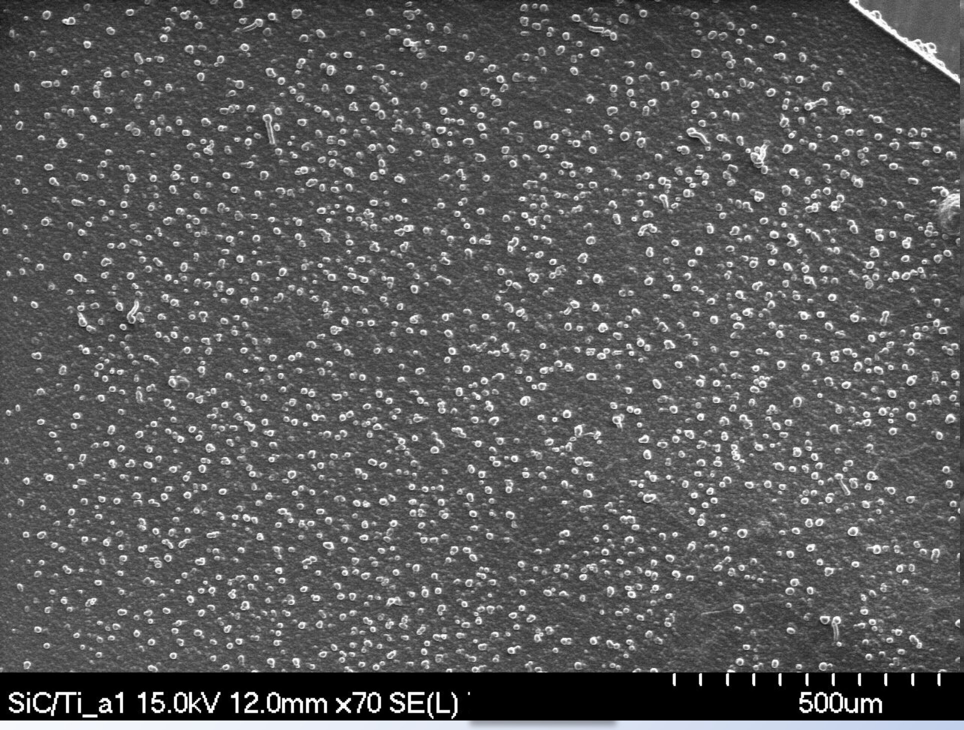
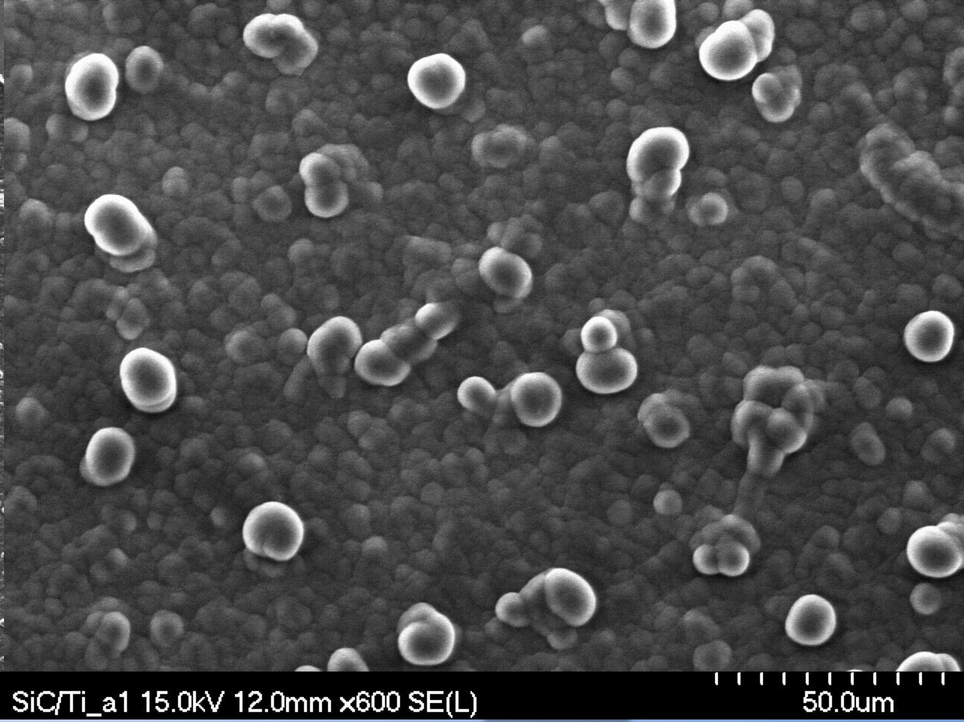


SiC varies in surface
chemistry and surface roughness


catalyst
substrate
Ostwald ripening
Tip growth
Base growth





Catalyst “film” following heat treatment at synthesis temperatures

Major Processing Difference between CNT and BNNT -

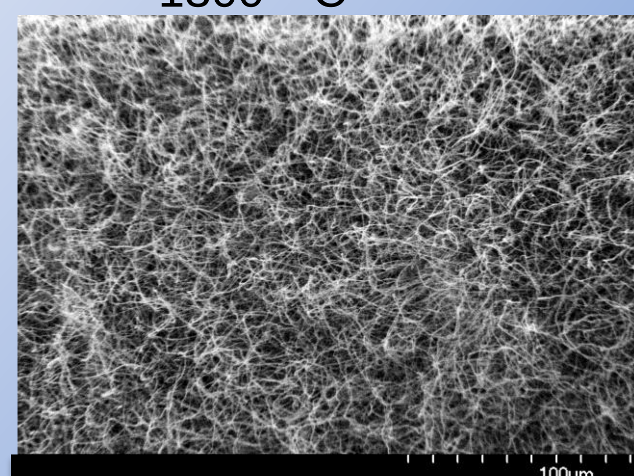
	CNT	BNNT
Processing temperatures	625° C VACNT	1200 -1400° C

Mobility of the catalyst upon the substrate, or the substrate acting as a catalyst, becomes problematic as processing temperature increases.

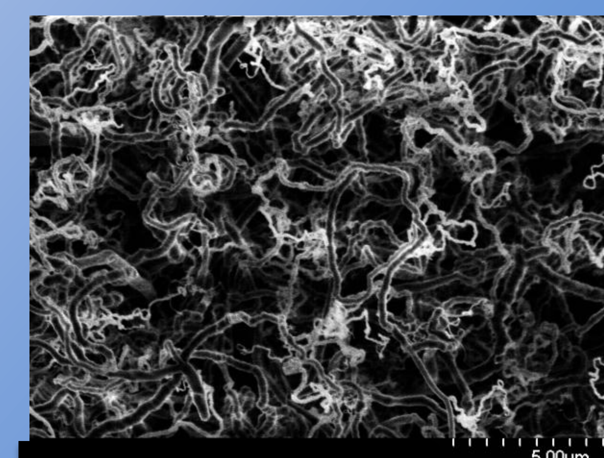
Tip growth becomes more likely

1200° C

1300° C

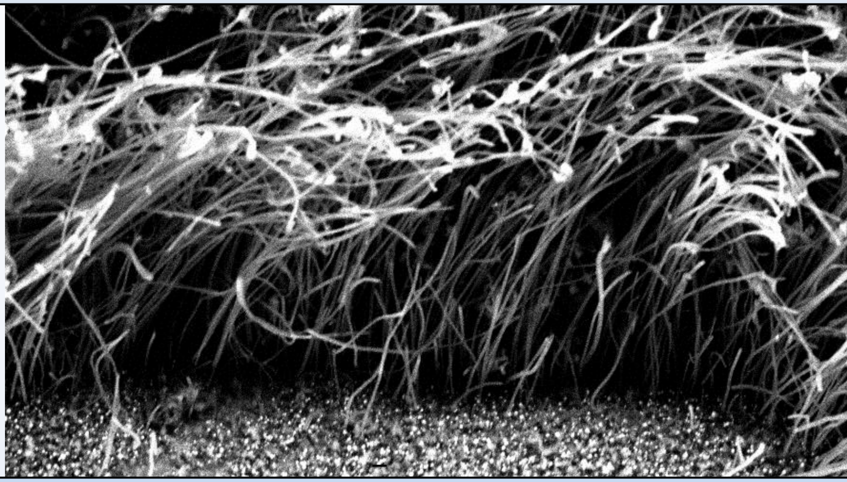


1400° C

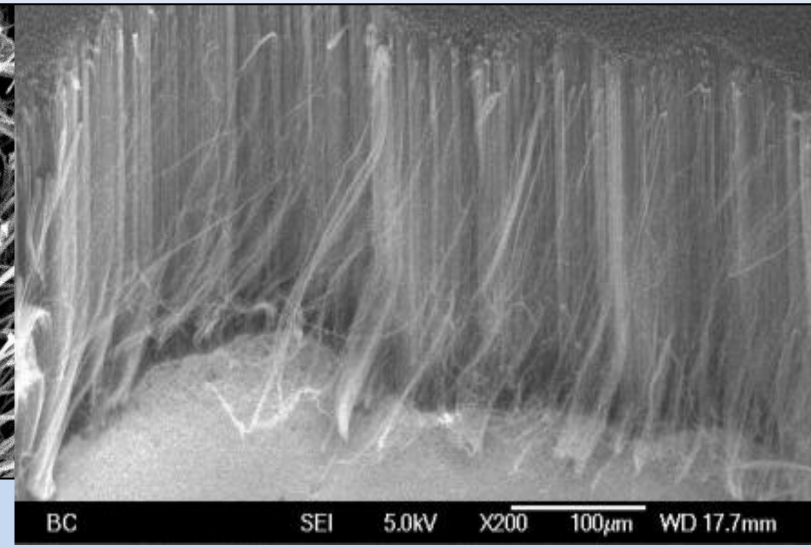


Aligned Boron Nitride Nanotube Forests for Thermal Management

BNNT on SiC surfaces demonstrated



20 µm

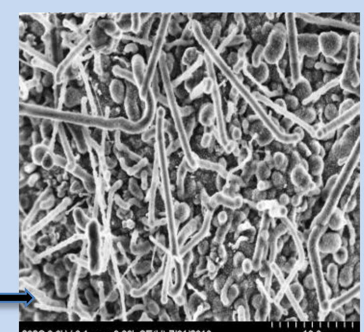


NASA GRC –
Aligned BNNT forest:

- Shorter nanotubes and less well aligned than CNT– but demonstrates feasibility
- Need to improved catalyst deposition

Nanolab –
Commercial CNT nanoforest marketing photo

Beginning of non-aligned BNNT growth



Aligned Boron Nitride Nanotube Forests for Thermal Management

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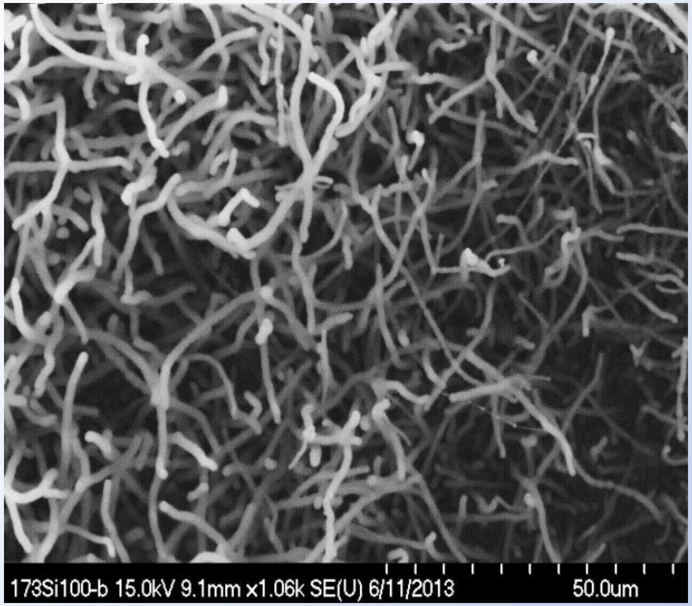
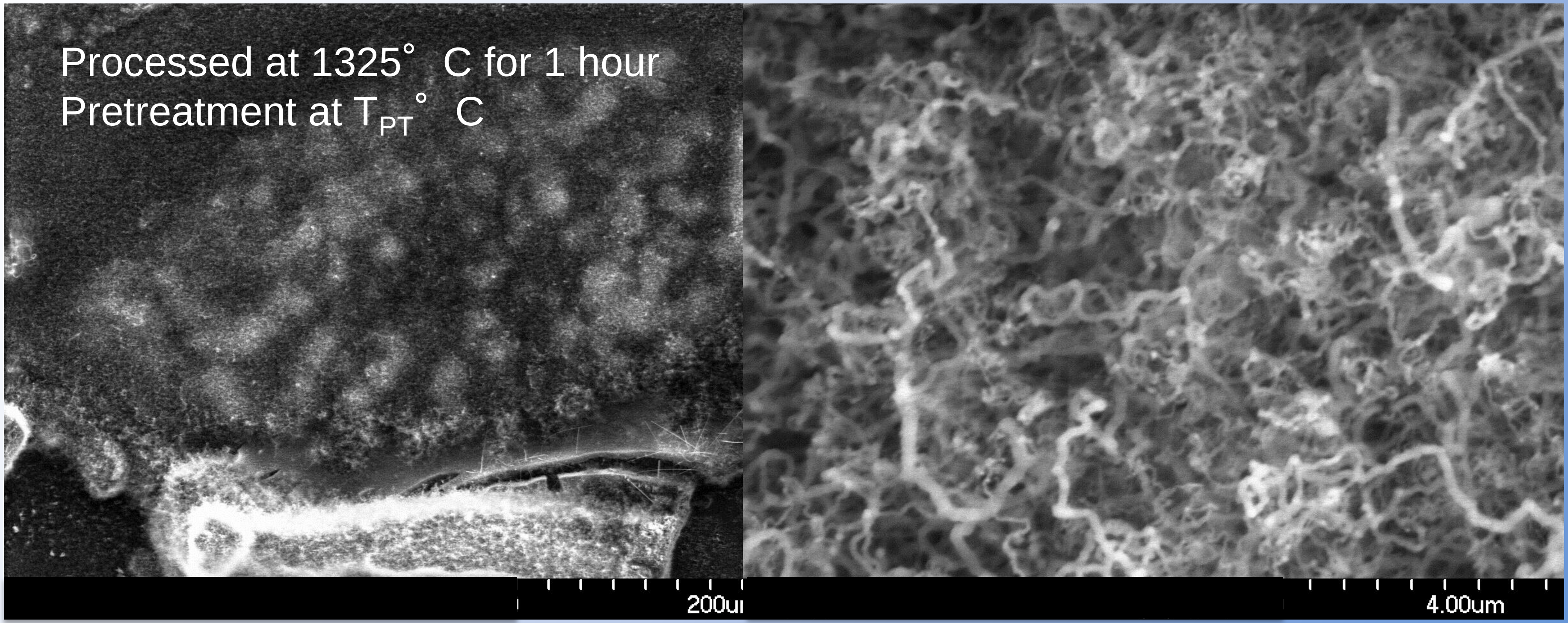
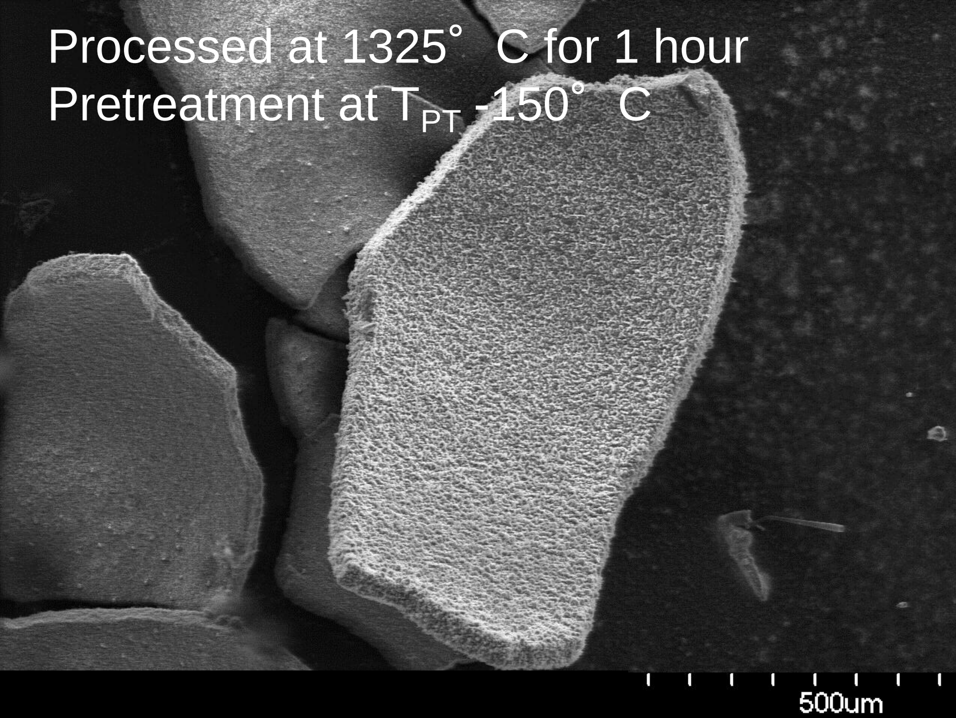
BNNT on Si surfaces demonstrated

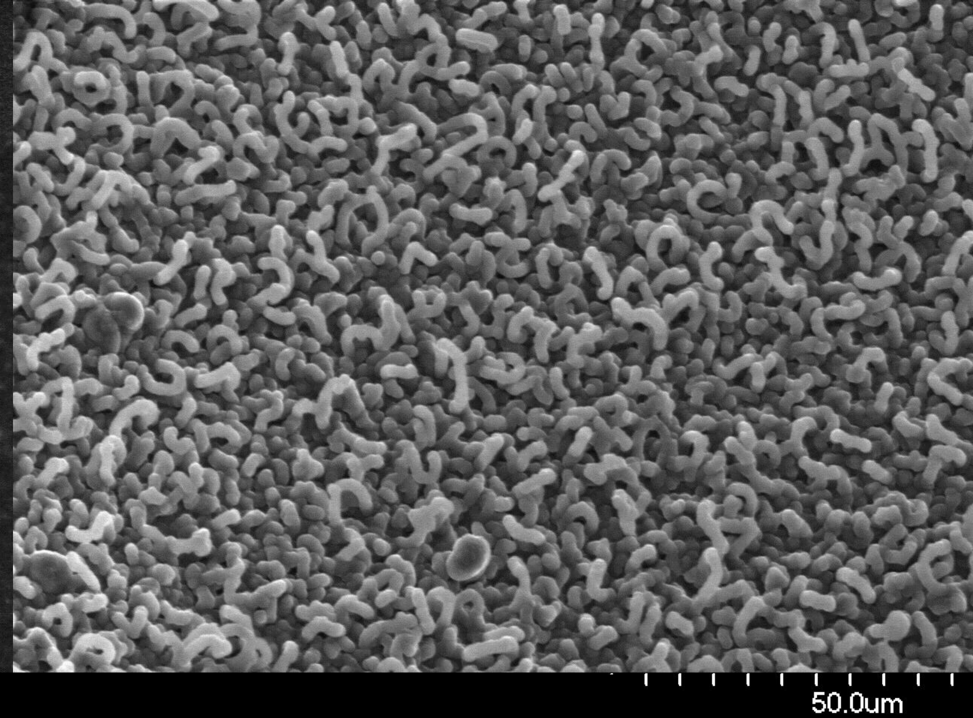


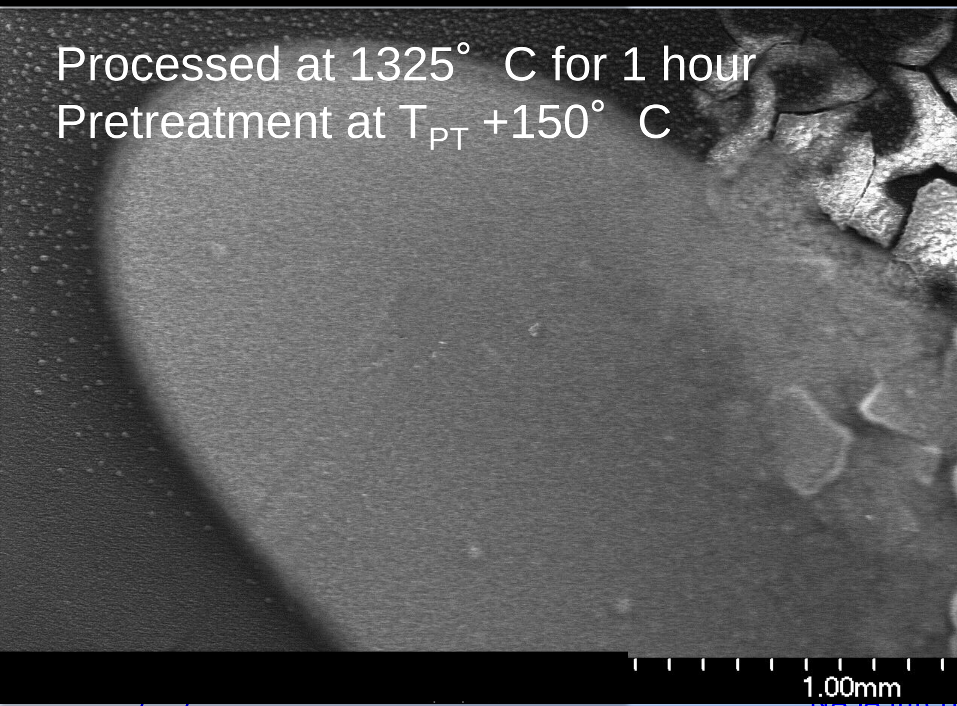
- Si (100) surface and (111) surface grow BN similarly.
- BNNT growth seems to be independent of the crystal orientation.
- The implication: a polycrystalline surface will grow BNNT similarly.
- Single crystal is not necessary.
- Semi-aligned growth occurs easily.
- Catalyst mobility is an issue for aligned growth
- Need to reduce synthesis temperature

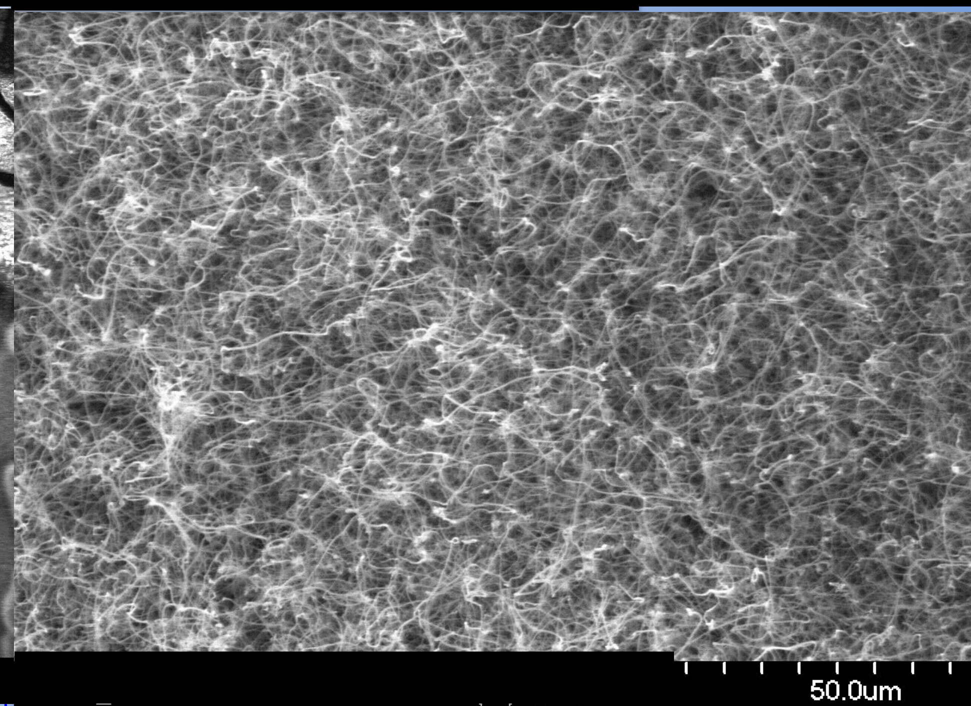
Pretreatments are Effective Methods of Morphology Control




Processed at 1325° C for 1 hour
Pretreatment at T_{PT} -150° C
500um


50.0um


Processed at 1325° C for 1 hour
Pretreatment at T_{PT} +150° C
1.00mm

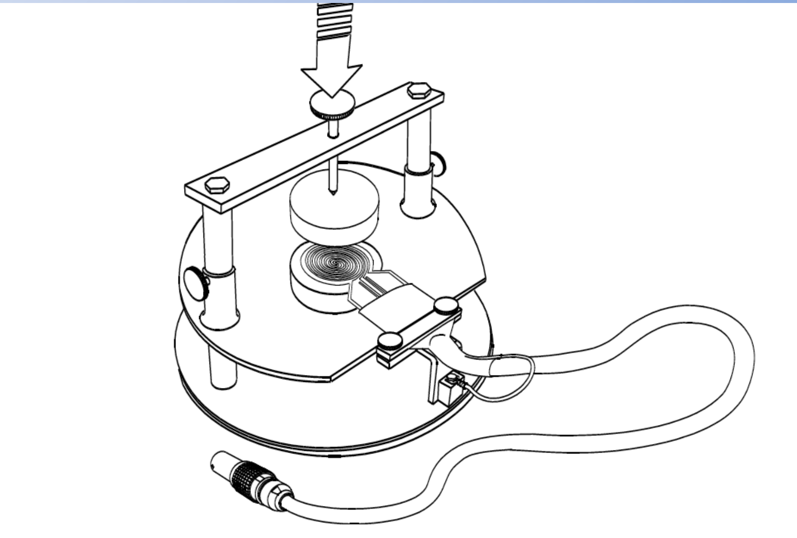

50.0um

Thermal Conductivity Measurements

Methods –

laser or light flash – not suitable for porous materials.

Hot Disk Transient Plane Source – procured and in place – Dr Fran Hurwitz is the lead.



Hot Disk Transient Plane Source (ISO/DIS 22007-2.0)

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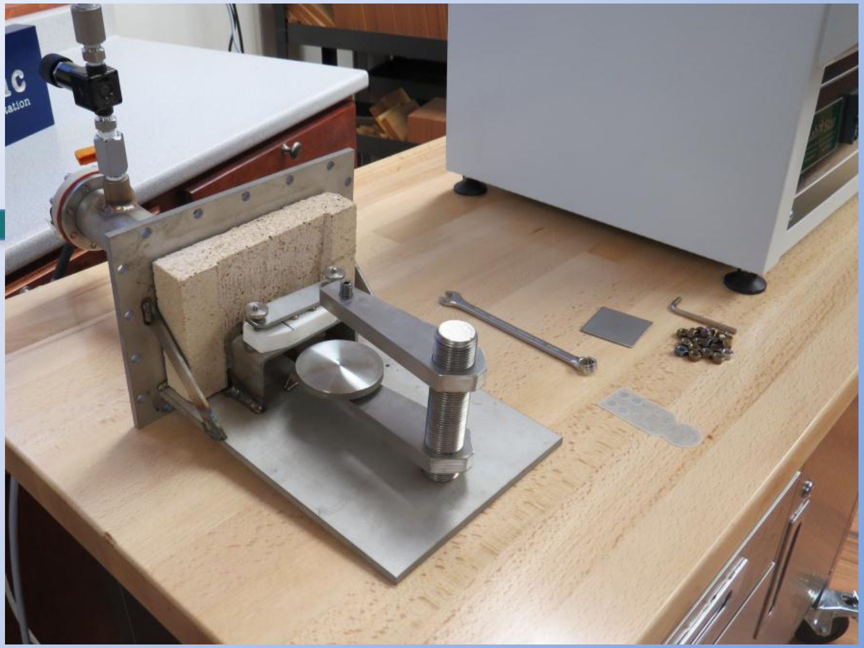
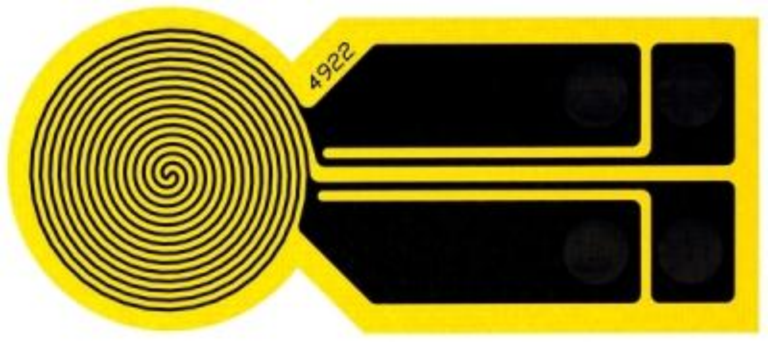


- Instrument has been received and is being installed.
- Measurements will be initiated at ambient temperature on materials for which we have thermal properties obtained by other techniques so as to establish test parameters suitable to low thermal conductivity samples and to establish data reliability.
- Furnace fixturing limits sample diameter to 60 mm, requiring some adjustment of parameters for high temperature measurement.
- Capabilities will include inert atmosphere



Aligned Boron Nitride Nanotube Forests for Thermal Management

Desired Outcome - Evaluate feasibility of BNNT forest growth

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From Nanolab website -

NASA GRC BNNT forests

Features	PECVD	Thermal CVD	NASA GRC BNNT forests
Diameter, nm	30-150	1-2 (SWNT) 5-30 (MWNT)	Thermal CVD MWNT 8-100
Length, microns	1-20	5-500	1-10 | (5-1000)
Rigidity	Freestanding (bed of nails)	Mutually Supported	Mutually supported
Site Density CNT/cm^2	10^5 to 10^9	10^{10} to 10^{11}	varies
Substrates	Si, SiO_2, W, Mo, SS, C	Si, SiO_2, SS, Ti, mica	SS, Si, C, Al_2O_3
Adhesion Layer	Ti or Cr, 100nm	Al_2O_3	
Catalyst	Nickel	Iron	Fe, oxide, others
Size	up to 2" square	up to 1.25" x 4"	~1/2"x1/2"| (2"X4")
Patterns	Yes, lithographic	Yes, lithographic	yes
Uses	field emission devices, sensors, electrostatically actuated devices, etc	supercapacitors, electrodes, optical coatings, heat transfer, etc.	Heat transfer, etc

Issues/lessons learned

BNNT synthesis temperatures impact catalyst size/densities, initially causing larger BNNT diameters and tip growth
This may not be an issue for heat transfer applications.

Semi-aligned growth is “straightforward”. Must be optimized for each matrix
Need to determine need for nanotube alignment for particular applications

Common engineering materials are catalysts for BNNT growth.
Limiting BNNT growth may be necessary in some cases.

Difficulty measuring thermal conductivity in forests.

Lots to learn in this system, this effort is just a beginning.

Conclusions

- Established the feasibility of BNNT aligned forest growth
- Identified critical issues for BNNT forest growth
  - High temperatures – Ostwald ripening of catalyst particles
  - Interaction of matrix/catalyst – need to restrict mobility of nano-catalyst particles to achieve base growth. Otherwise tip growth
  - Lowered BNNT synthesis temperature by 100 C

- Identify path for development of BNNT forests – Phase 2 effort
  - Increase BNNT growth by increasing base growth
  - Pretreatment of nano-catalyst particles on substrate materials. Oxidation/reducing environments
  - Additional design changes on rig 2 – to reduce dwell/temp/catalyst growth

Distribution/Dissemination

- Presentation at International Conference on Nanotube Science and Technology (NT14) will be made, Los Angles, CA. “ Aligned Nanoforest BNNT Growth”, Janet Hurst, Ching-cheh Hung, and Diana Santiago.
- Journal article draft is underway
- Invention disclosure will be filed on processing/details of catalysts
- Invention disclosure on equipment is being prepared

Next steps

- Additional changes to the processing equipment are now underway to further improve uniformity - invention disclosure to be filed on equipment.
- Invention disclosures to be filed on processing/catalysts/pretreatments
- Following the above equipment modification – a 4^{th}, more extensive equipment modification is anticipated.
- Pre-treatments of catalysts and other methods of slowing NT growth and reducing catalyst mobility
- Focus on one matrix/catalyst system with multiple catalyst treatments
- Thermal conductivity measurements remain to be made.
- Would like to find a demonstration system

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